Physicochemical and thermal study of a MPCM of PMMA shell and paraffin wax as a core

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Abstract

The present work studies a Phase Change Slurry (PCS) as a proposed Thermal Energy Storage (TES) medium. Microencapsulation is an advanced technology to implement PCMs (Phase Change Material) avoiding leakage from building materials. The morphology and physicochemical properties of this Microencapsulated Phase Change Material (MPCM) sample were analyzed using some analytical techniques like Scanning Electron Microscopy (SEM), Infrared Spectroscopy (FT-IR), Thermogravimetrical Analysis (TGA), Differential Scanning Calorimeter (DSC), and Atomic Force Microscopy (AFM). The results showed that Micronal® DS 5007 is a suitable candidate to be used as slurry in active systems due to their studied mechanical properties.

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Keywords: Microencapsulated Phase Change Material; Phase Change Slurry; PSD; SEM; FTIR; TGA; DSC; AFM

1. Introduction

Phase Change Materials (PCM) are commonly contained in microcapsules in order to avoid the leakage, and conserve the efficiency of the thermophysical properties when they are implemented in slurry active systems [1]. These microcapsules comprise a polymeric shell where a PCM, usually a paraffinic one, is contained at the core. PCM have been developed in slurries form to improve the heat transfer rate of the carrier fluid, obtaining the Phase Change Slurries (PCS). There are several applications where PCS can be implemented such as heating [1],

refrigeration [2], air-conditioning [3], heat exchangers [4], and ventilation [5]. It is well known that there are physicochemical changes on this type of PCS after several thermal cycles [6]. These changes are attributed to a partial degradation of the microcapsules by breakage [7]. For this purpose, physicochemical, thermophysical and mechanical properties of Micronal® DS 5007 are studied in this paper. Micronal® DS 5007 from BASF® consist on a suspension of water and microcapsules (5:2). Moreover, the structure and the physicochemical properties of the slurries will define the final application. Therefore, the main objective of this paper is to study the mechanical performance of this Microencapsulated Phase Change Material (MPCM) to be applied as PCS for their use in active systems.

2. Materials and methodology

Micronal® DS 5007 is a PCS which is normally used in active systems. To characterize this sample deeply, Fourier Transformed Infrared Spectroscopy (FT-IR) was used to characterize the polymeric shell of this PCS with a Spectrum Two™ from Perkin Elmer. Microcapsules' size and morphology were studied evaluating the Particle Size Distribution (PSD) using a Beckman Coulter® LSTM 13 320, and microcapsules were observed with Scanning Electron Microscopy (SEM) using a Jeol JSM-6510.

Thermal stability of the samples was evaluated with a Simultaneous SDTQ600 TA Instruments device under dried air atmosphere. The scanning rate of the Thermogravimetrical Analysis (TGA) used was 0.5 $K\cdot min^{-1}$ in the temperature range between 25 and 30 ºC. Then, temperature was increased under 1 $K\cdot min^{-1}$ heating rate from 30 to 100 ºC and 5 $K\cdot min^{-1}$ from 100 to 600 ºC. Hyphenated technique is used coupling a FT-IR detector in the TGA gas output to analyze the gradation products. In addition, Differential Scanning Calorimetry (DSC) was used to analyze the melting temperature and the melting enthalpy of PCM between 10 ºC and 40 ºC, applying 0.5 $K\cdot min^{-1}$ dynamic mode, following the study of Barreneche *et al.* [8] using a DS 822e by Mettler Toledo. Finally, Atomic Force Microscopy (AFM) was performed to determine the force that has to be applied to break the shell of the Micronal® DS5007 MPCM with a Peak Force Quantitative Nanomechanics mode (QNM), with a diamond probe from Bruker which has 388 $Nn\cdot nm^{-1}$ spring constant.

3. Results and discussion

3.1. Physicochemical and thermophysical characterization

3.1.1. Size and morphology of MPCM

The PSD in volume shows unimodal distribution of particle size ranging in the interval between 2 and 12 μm. The average diameter of the PCS was 4.880 μm as it can be observed in Fig. 1.

Furthermore, MPCM morphology was analyzed by Scanning Electron Microscopy (SEM), the sample under study was pretreated by drying the microcapsules at room temperature before its observation. The size morphological results of the Micronal® DS 5007 show that the capsules are roughly 5 μm diameter as it is observed in Figure 2a, which agree with the PSD results. Besides, the wall thickness was estimated for broken microcapsules (deformed by compaction) showing a thickness around 0.5 μm (Figure 2b).

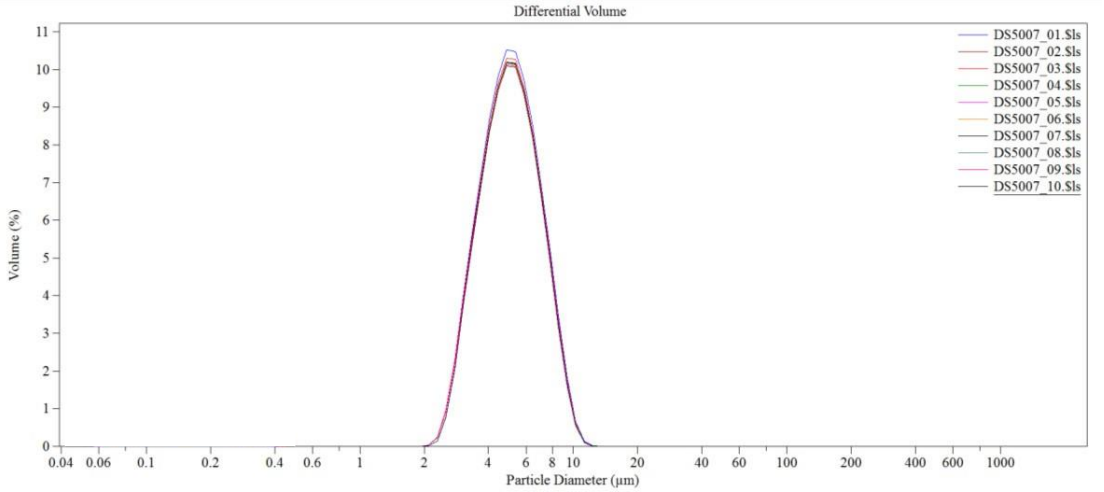

Fig. 1. Particle Size Distribution (PSD) of Micronal® DS 5007.

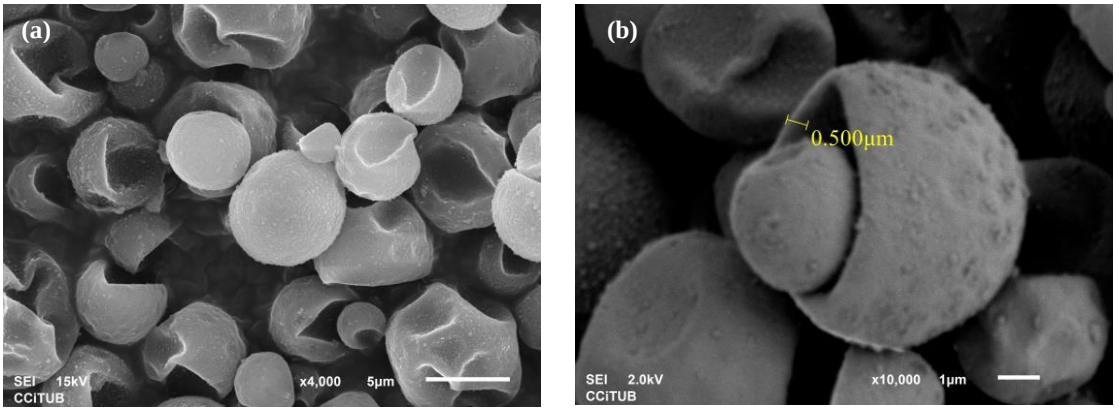

Fig. 2. Scanning Electron Microscopy (SEM) images of Micronal® DS 5007 (a) shape and size of the microcapsules; (b) wall shell thickness.

3.1.2. Chemical characterization

Chemical characterization of the shell was performed with Fourier-Transformed Infrared (FT-IR) by Attenuated Total Reflectance (ATR), which was used to characterize the most important peaks for the polymeric shell of the MPCM. Table 1 lists the characteristic peaks found. Thereby, these peaks correspond to an acrylic polymer like PMMA.

Table 1. FT-IR characteristic peaks obtained from MPCM shell.

FTIR Peak (cm^{-1})	3368.9	2920.9	2852.0	1729.5	1466.6	1123.5	720.5
Attributed to	aqueous suspension	aliphatic C-H stretching vibration	aliphatic C-H stretching vibration	ester carbonyl group stretching vibration	C-H bending vibration	C-O stretching vibration of the ester group	C-H bending

3.1.3. Thermal stability

The thermal degradation of Micronal® DS 5007 sample was evaluated and three processes from TGA results were observed, as it is shown in Figure 3. The first weight loss from 25 ºC to 93.9 ºC is due to the water content of the PCS, and it corresponds to 65.60 % wt. The second one from 93.9 ºC to 245.1 ºC confirms the presence of the paraffin wax contained inside the shell, and it represents the 65.73 % wt. of the dry sample. Finally, the third weight loss from 245.1 ºC to 408.6 ºC is due to the acrylic shell [9], and the thermal degradation contributes on 19.36 % wt. of the dry sample. The wall shell degradation step is the last one and it starts after the microcapsule degradation. The total residue of the dry sample is 14.91 % wt.

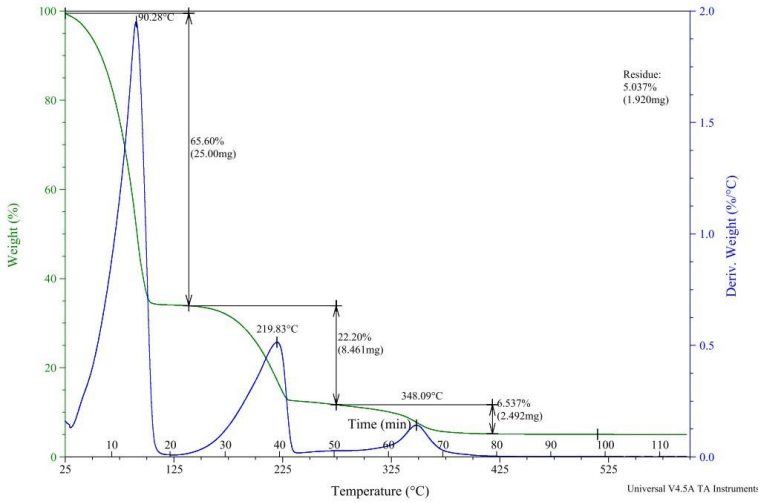

Fig. 3. Thermogravimetrical Analysis (TGA) of the PCS Micronal® DS 5007.

After coupling the TGA with the FT-IR, the gas was analyzed over time and 0 s, 1900 s, 3400 s, and 7600 s spectra are shown in Fig. 4. As it is observed in this figure, there are two different signals on the FT-IR spectra: at the beginning and at the end of the analysis (0 s and 7600 s) there were not characteristic peaks, and it can be observed that at 1900 s and 3400 s the corresponding peaks of functional groups resulting from the thermal degradation of an acrylic polymer.

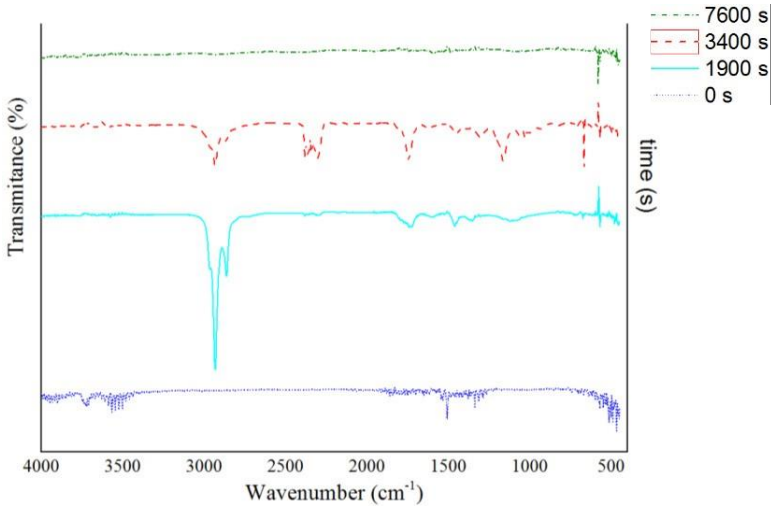

Fig. 4. FT-IR gas analysis from a calcinated Micronal® DS 5007 sample of TGA

3.1.4. Differential Scanning Calorimetry (DSC)

The results obtained from DSC analysis were 98.3 kJ· kg^{-1} and 75.8 kJ· kg^{-1} for the melting enthalpy and solidification enthalpy, respectively. Thereby, the sample studied with DSC contemplates all the system composed by water-dispersant/shell/PCM. The results were not repeatable due to the difficulty of taking a homogeneous PCS aliquot.

Moreover, the melting temperature obtained for this PCS is 23.4 ºC and the solidification temperature is 22.3 ºC (both between 14-24 ºC).

3.2. Stiffness characterization

Several experiments were carried out using Atomic Force Microscopy in nanoindentation mode [10] to evaluate the required force to break the microcapsules to use it in active systems. In addition, effective Young's Modulus (E_{eff}) at different temperatures (23 ºC and 45 ºC) was evaluated in order to distinguish the mechanical MPCM behavior when the PCM is melted and solidified.

The main results obtained are shown in Fig. 5 and 6, where it is shown that the fracture load for the microcapsules at 23 ºC was 11 µN, and 1.7 µN at 45 ºC. The deflection error is proportional to the applied force.

Furthermore, the shape of the MPCM changes when Micronal® DS 5007 is heated up, producing an expansion of the microcapsule, as it can be observed in Fig. 7.

Moreover, effective Young's modulus (E_{eff}) mapping is shown in Fig. 8 at 0.5 kHz per second. The flatter area studied was 10 x10 µm MPCM region at 23 ºC.

Besides, the deformation histogram is evaluated in Fig. 8 and a deformation from 10 to 20 nm with a great distribution of values is observed. The *y* axis represents the total pixels amounts for this area, and a 0.1 % of the total pixels belong to the results. Moreover, when a vertical force of 500 nN is applied on the top of the MPCM, the E_{eff} value was 200 MPa.

Furthermore, the same study was performed at 45 ºC, and it is shown in Fig. 9. In this case, the deformation histogram was given between 5 to 30 nm, and the result of the E_{eff} histogram applying 500 nN was 50 MPa, four times lower due to the softening of the polymer as well as liquid state of PCM.

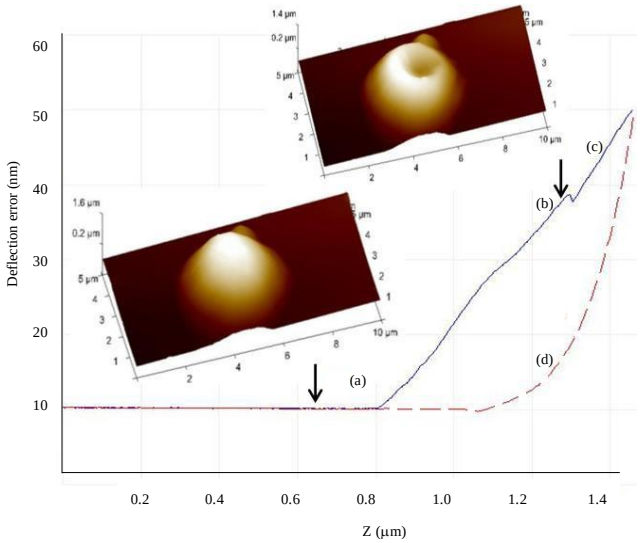

Fig. 5. Topographic Atomic Force Microscopy (AFM) images for Micronal® DS 5007 at 23 ºC, (a) unbroken microcapsule; (b) plastic penetration where the fracture load was 11 µN; (c) deformation of the sample; and (d) unbroken microcapsule. The solid line was the deflection error (nm), and the dotted line was the retraction of the AFM probe.

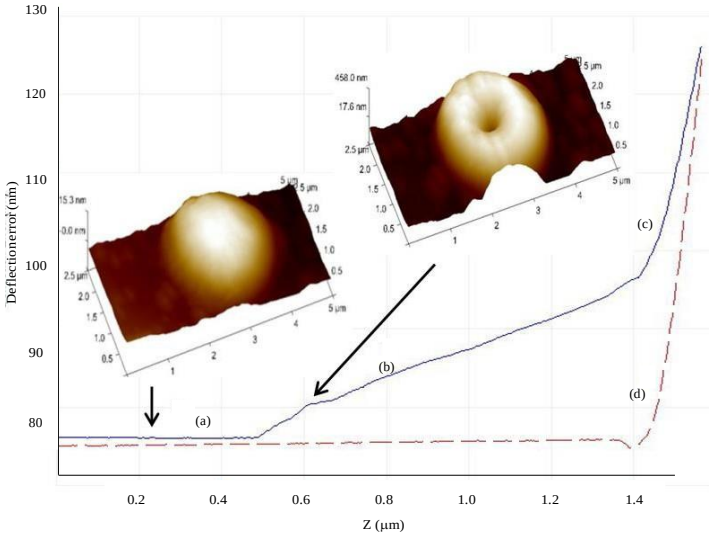

Fig. 6. Topographic Atomic Force Microscopy (AFM) images for Micronal® DS 5007 at 45 ºC, (a) unbroken microcapsule; (b) fracture load of 1.7 µN in the plastic penetration; (c) deformation of the sample; and (d) unbroken microcapsule. The solid line was the deflection error (nm), and the dotted line was the retraction of the AFM probe.

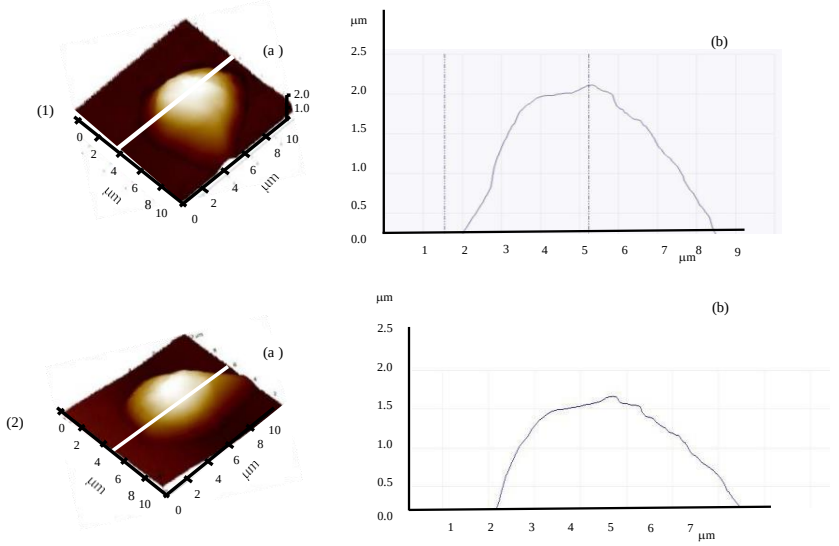

Fig. 7. Micronal® DS 5007's sample at (1) 23 ºC and, (2) 45 ºC; (a) 3D view, and (b) topographic image of 10x10 µm

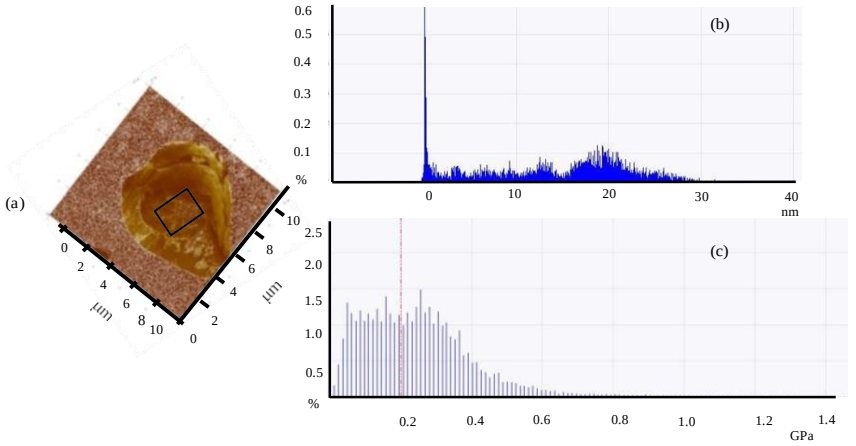

Fig. 8. Effective Young's modulus (E_{eff}) mapping of Micronal® DS 5007 at 23 ºC; (a) 3D view; (b) Deformation histogram; (c) E histogram.

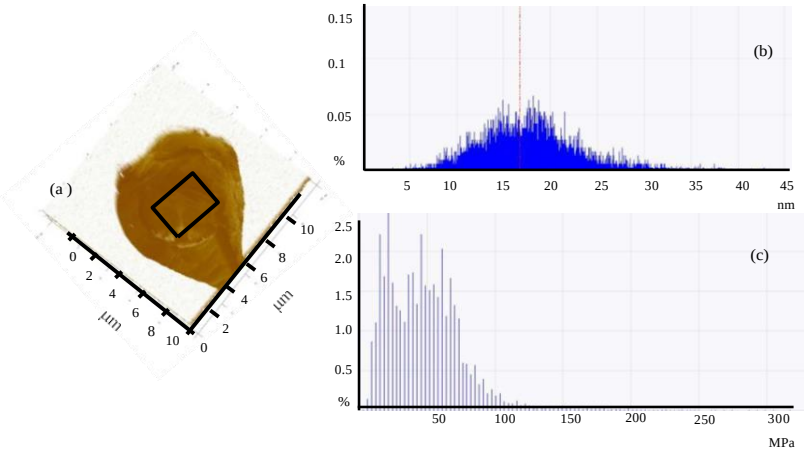

Fig. 9. Effective Young's modulus (E_{eff}) mapping for Micronal® DS 5007 at 45 ºC; (a) 3D view; (b) Deformation histogram; (c) E histogram

4. Conclusions

The PCS Micronal® DS 5007 consists on paraffin PCM core and PMMA as a shell as FT-IR results showed. The study of the size and morphology of the microcapsules reveal spherical particles of 5 µm diameter and 0.5 µm wall shell thickness. The thermal degradation was observed in three steps. Moreover, the required applied load in order to break the sample was not constant and it depends on the working temperature. Hence, the temperature is a key point to take into account considering these systems.

In summary, from the mechanical point of view, acrylate groups to be used as a shell of microcapsules are a suitable choice for TES active systems for the obtained results in this paper.

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